Thermochimica Acta, 197 (1992) 201–210
Elsevier Science Publishers B.V., Amsterdam

Thermochemistry of complexes of pyridine and picolines with phenyldihaloarsines

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(Received 18 June 1991)

Abstract

The complexes $PhAsX_2 \cdot L$, where L = pyridine (py), β- or γ-picoline (β- or γ-pico) and X = Cl, Br or I, were synthesized and characterized by melting point, elemental analysis, thermogravimetric studies and infrared spectroscopy. The standard enthalpies ($\Delta_r H^{\ominus}$) for the Lewis acid/base reactions were determined from the enthalpies of dissolution in 25% ethanolamine in ethanol of the complexes, phenyldihaloarsines and ligands at 298.15 K. The following thermochemical parameters for the complexes were calculated from $\Delta_r H^{\ominus}$ values and thermochemical cycles: the standard enthalpies of formation ($\Delta_f H^{\ominus}$), the standard enthalpies of decomposition ($\Delta_D H^{\ominus}$), the lattice standard enthalpies ($\Delta_M H^{\ominus}$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^{\ominus}(g)$). The mean standard enthalpies of arsenic–nitrogen bonds ($\bar{D}$(As–N)) were estimated.

INTRODUCTION

The mean arsenic–nitrogen coordinate bond energies for a series of complexes of pyridine and picolines with arsenic trihalides have been recently determined [1]. This paper describes the interaction of phenyldihaloarsines with the same bases. The mean arsenic–nitrogen bond energies in the trihalide complexes range from 121 to 168 kJ mol^{-1} [1]. The substitution of one halogen atom by a phenyl group in the arsenic trihalide results in the formation of solid complexes which were submitted to calorimetric measurements in order to determine the influence of this substitution on the mean As–N bond energies.

EXPERIMENTAL

All preparations were carried out in polyethylene glove bags under a nitrogen atmosphere.

Chemicals

The phenyldihaloarsines were prepared from phenylarsonic acid [2,3] using methods outlined in the literature [4–6]. Solvents and ligands used in the synthesis of complexes were purified by distillation and stored over Linde 4-A molecular sieves.

Analytical

Carbon, hydrogen and nitrogen were determined by microanalytical procedures. The halogen contents were measured by potentiometric titration using standard 0.1 N $AgNO_3$ solution [7] after the adducts had been dissolved in water. The arsenic content was determined by redox titration of solutions of the complex samples with standard 0.05 N iodine solution until the appearance of the blue color of the starch indicator [8].

Complex synthesis

The complexes were prepared by the reaction in solution of the phenyldihaloarsines and the ligands. A typical procedure is given below for $PhAsCl_2 \cdot py$.

To a solution of 2.0 ml of $PhAsCl_2$ (14.8 mmol) in 20 ml of petroleum ether–*n*-hexane (1 : 1 by volume), 1.2 ml of pyridine (14.8 mmol) dissolved in 20 ml of petroleum ether was added slowly, drop-wise with stirring, under a flow of dry nitrogen. Stirring was maintained for at least three hours. The white solid formed was filtered, washed with three 10 ml portions of petroleum ether (always under flowing dry nitrogen) and then dried for several hours in vacuo. The compound obtained was stored in a desiccator over calcium chloride. For the phenyldiiodoarsine complexes, a molar ratio of 1 : 2 was used because the 1 : 1 molar ratio yielded an oily non-crystalline product.

Infrared spectra

These were obtained on a Perkin–Elmer 180 spectrophotometer using sample mulls in nujol sandwiched between KBr plates for the complexes, and using a liquid cell with NaCl windows for the ligands and arsines.

Thermogravimetric studies

These were made under nitrogen atmosphere using a Du Pont 1090 thermogravimetric analyzer with samples varying in weight from 2.16 to 14.45 mg and a heating rate of 10 K min^{-1}

Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described before [1,9].

RESULTS AND DISCUSSION

Nearly all the adducts were prepared using a molar ratio of 1 : 1 between the $PhAsX_2$ and the ligands. However, a molar ratio of 1 : 2 was used in the preparation of the $PhAsI_2$ and $PhAsCl_2$ complexes of β-picoline because oily products were obtained with a 1 : 1 molar ratio. The $PhAsI_2$ complexes obtained were solids; $PhAsCl_2 \cdot \beta$-pico was obtained as a white paste. Attempts to synthesize complexes of $PhAsX_2$ with α-picoline ligand were unsuccessful. The yields of the compounds range from 52% to 100%. The melting points, colors, appearance and analytical data for the complexes are summarized in Table 1.

Infrared data

The infrared spectra of the pyridine complexes showed dislocations and intensity decreases for some bands when compared with the spectrum of free pyridine. The stretching of the As–C(phenyl) bond [10] was situated in the 1076–1070 cm^{-1} region. Coordinated pyridine is distinguished from free pyridine by the presence of a new band in the 1250–1200 cm^{-1} region [11]; this was observed in the pyridine complexes synthesized here.

The infrared spectra of the γ- and β-picoline complexes showed dislocations of several bands with respect to the free ligands. The ν(As–C(phenyl)) bond frequencies, found in the 1076–1070 cm^{-1} region for the free arsines [10], were shifted towards higher frequencies in the complexes. The infrared data can be interpreted in terms of coordination of the ligands to the arsines [12,13]. The main infrared bands of the ligands and the adducts, as well as their assignments, are presented in Tables 2–4.

Thermogravimetric data

The thermogravimetric behavior of the adducts was similar. Nearly all of the complexes lose ligand and arsine together in a single step. For adducts of phenyldi-iodoarsine with pyridine, two steps were observed; the first with elimination of part of the ligand and the second with elimination of the rest of the ligand and the arsine. All the adducts are unstable in the liquid phase. The thermoanalytical data of the adducts are presented in Table 5.

TABLE 1

Melting points, appearance, yield and analytical data of the complexes

Compound	MP[a] (°C)	Appearance[b]	Yield (%)	C (%)		H (%)		N (%)		As (%)		Halogen (%)	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$PhAsCl_2 \cdot py$	77–8	s.y. gr.cr.	100	43.74	43.26	3.34	3.49	4.64	4.80	24.81	24.85	23.48	23.40
$PhAsCl_2 \cdot \gamma$-pico	121–2	wh.cr.	48	45.60	45.52	3.83	3.84	4.43	4.30	23.70	23.87	22.43	22.31
$PhAsCl_2 \cdot \beta$-pico	n.o.	wh.p.	72	45.60	45.41	3.83	4.03	4.43	4.56	23.70	23.54	22.43	22.45
$PhAsBr_2 \cdot py$	88	ye.pw.	52	33.80	33.65	2.58	2.56	3.58	3.69	19.16	19.24	40.88	40.67
$PhAsBr_2 \cdot \gamma$-pico	96	ye.pw.	63	35.59	35.43	2.99	2.84	3.46	3.42	18.50	18.62	39.46	39.57
$PhAsBr_2 \cdot \beta$-pico	78	ye.pw.	73	35.59	35.62	2.99	2.87	3.46	3.62	18.50	18.61	39.46	39.50
$PhAsI_2 \cdot py$	150	br.pw.	54	27.25	27.22	2.08	2.15	2.89	2.71	15.45	15.35	52.34	52.52
$PhAsI_2 \cdot \gamma$-pico	87	br.pw.	79	28.89	28.92	2.42	2.57	2.81	2.72	15.02	15.03	50.87	50.67

[a] Uncorrected; n.o., not observed.

[b] Wh., white; ye., yellow; br., brown; gr., green; y., yellowish; s., slightly; cr., crystals; pw., powder; p., paste.

TABLE 2

Assignment of infrared frequencies (cm^{-1}) of py and its complexes [a]

py	$PhAsCl_2 \cdot py$	$PhAsBr_2 \cdot py$	$PhAsI_2 \cdot py$	Assignment
1590 sh	1613 s	1595 m	1638 w	ν(CC)
1577 vs	n.o.	n.o.	1602 w	ν(CC)
1480 s	1490 s	1520 m,b	1530 m	ν(CC, CN)
1435 vs	1438 s	n.o.	n.o.	ν(CC, CN)
1355 sh	1340 m	n.o.	1330 w	ν(CC, CN)
	1250 m	1257 m	1237 w	
1212 s	1203 m	n.o.	n.o.	β(CH)
1142 s	1158 s	1150 w	n.o.	ν(CC, CN)
	1078 s	1068 w	1075 w	ν(As–C)
1063 s	1060 s	1060 w	1083 w	β(CH)
1027 s	1025 s	1012 m	1025 m	ring
990 s	1000 s	885 w	n.o.	ring
940 w	930 s	n.o.	n.o.	γ(CH)
747 vs	n.o.	742 w	n.o.	ϕ(CC)
	740 s	730 s	730 m	γ(CH(Ph))
677 sh	680 s	670 s	670 m	ϕ(CC)
598 s	607 s	n.o.	n.o.	α(CCC)

[a] Intensity of bands: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad. Key: n.o., not observed; ν, stretching; β, bending in plane; γ, bending out of plane; α, ring deformation in plane; ϕ, ring deformation out of plane; ring, ring breathing; R, rocking; a, antisymmetric; s, symmetric; Ph, phenyl group.

TABLE 3

Assignment of infrared frequencies (cm^{-1}) of γ-pico and its complexes [a]

γ-pico	$PhAsCl_2 \cdot \gamma$-pico	$PhAsBr_2 \cdot \gamma$-pico	$PhAsI_2 \cdot \gamma$-pico	Assignment
1600 vs	1608 s	1598 m	1628 m	ν(CC)
1560 s	1558 s	1548 w	1590 m	ν(CC)
1445 vs	1433 s	n.o.	n.o.	ν(CC, CN)
1410 vs	n.o.	n.o.	n.o.	$\nu_a(CH_3)$
1378 s	n.o.	n.o.	n.o.	ν(CC, CN)
1350 sh	n.o.	n.o.	1330 w	$\nu_s(CH_3)$
1292 w	1300 w	1305 m	1290 m	ν(CC, CN)
1218 s	1228 s	n.o.	1230 w	ring
n.o.	1196 m	n.o.	1187 m	β(CH)
n.o.	n.o.	n.o.	1160 m	β(CH)
	1076 s	1063 w	1070 m	ν(As–C)
1087 m	n.o.	1090 w	n.o.	β(CH)
1067 m	1058 m	1055 w	n.o.	β(CH)
1038 s	n.o.	n.o.	1010 m	$R(CH_3)$
995 s	996 m	990 w	n.o.	ring
798 vs	798 m	780 s	773 m	γ(CH)
	738 vs	738 s	725 m	γ(CH(Ph))
n.o.	688 s	682 s	n.o.	ϕ(CC)
665 w	660 m	662 s	657 m	ϕ(CC)

[a] See Table 2 footnote for key.

TABLE 4

Assignment of infrared frequencies (cm^{-1}) of β-pico and its complexes [a]

β-pico	PhAsCl$_2$·β-pico	PhAsBr$_2$·β-pico	Assignment
1578 sh	n.o.	1610 m	ν(CC)
1570 vs	1560 s	1570 w	ν(CC)
1473 vs	n.o.	n.o.	ν(CC, CN)
1448 vs	1438 s	n.o.	$\nu_a(CH_3)$
1408 vs	n.o.	n.o.	ν(CC, CN)
1378 s	n.o.	n.o.	$\nu_s(CH_3)$
1331 m	n.o.	1315 w	ν(CC, CN)
1223 m	1230 w	n.o.	ring
1185 s	1185 w	1175 m	β(CH)
	1078 m	1060 m	ν(As–C)
1036 sh	1025 w	1040 w	R(CH_3)
983 m	n.o.	992 m	ring
	740 s	740 s	γ(CH(Ph))
706 vs	695 s	718 s	ϕ(CC)
n.o.	680 s	688 s	ϕ(CC)
658 w	665 w	662 vs	α(CC)

[a] See Table 2 footnote for key.

TABLE 5

Thermoanalytical data of the compounds PhAsX$_2$·L

Compound	Weight loss (%)		Temperature range (K)	Species lost	MP (K)
	Calc.	Obs.			
PhAsCl$_2$·py	50.8	53.7	343–473	py 1/3PhAsCl$_2$	351
	49.2	41.3	473–667	2/3PhAsCl$_2$	
	0	4.1	667–1198		
PhAsCl$_2$·γ-pico	100	95.0	363–448	PhAsCl$_2$·γ-pico	395
	0	2.0	448–1198		
PhAsCl$_2$·β-pico	100	100	369–424	PhAsCl$_2$·β-pico	n.o.
	0	0	424–1198		
PhAsBr$_2$·py	100	94.7	322–449	PhAsBr$_2$·py	361
	0	0	449–1198		
PhAsBr$_2$·γ-pico	100	98.8	373–480	PhAsBr$_2$·γ-pico	369
	0	1.2	480–1198		
PhAsBr$_2$·β-pico	100	99.3	368–472	PhAsBr$_2$·β-pico	351
	0	0.7	472–1198		
PhAsI$_2$·py	6.4	6.2	340–358	1/5py	423
	93.6	94.1	358–515	4/5py·PhAsI$_2$	
	0	0	515–1198		
PhAsI$_2$·γ-pico	100	100	383–511	γ-pico·PhAsI$_2$	380
	0	0	511–1198		

TABLE 6

Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent [a]	Number of experiments	i	$\Delta_i H^{\ominus}$ (kJ mol^{-1})
py(l)	25% eth.EA	5	4	-0.65 ± 0.04
$PhAsCl_2$(l)	1:1 py:25% eth.EA	5	5	-153.39 ± 0.35
$PhAsCl_2 \cdot$py(s)	25% eth.EA	5	6	-101.15 ± 2.02
$PhAsCl_2$(l)	25% eth.EA	5	1	-158.93 ± 2.11
γ-pico(l)	1:1 $PhAsCl_2$:25% eth.EA	5	2	-1.02 ± 0.05
$PhAsCl_2 \cdot \gamma$-pico	25% eth.EA	5	3	-75.36 ± 0.62
$PhAsBr_2$(l)	25% eth.EA	5	1	-216.45 ± 0.82
py(l)	1:1 $PhAsBr_2$:25% eth.EA	5	2	-1.21 ± 0.11
$PhAsBr_2 \cdot$py(s)	25% eth.EA	5	3	-110.81 ± 0.50
γ-pico(l)	1:1 $PhAsBr_2$:25% eth.EA	5	2	-1.67 ± 0.10
$PhAsBr_2 \cdot \gamma$-pico(s)	25% eth.EA	5	3	-100.98 ± 0.15
β-pico(l)	1:1 $PhAsBr_2$:25% eth. EA	5	2	-0.57 ± 0.02
$PhAsBr_2 \cdot \beta$-pico(s)	25% eth.EA	5	3	-109.45 ± 1.97
$PhAsI_2$(l)	25% eth.EA	5	1	-176.11 ± 0.97
py(l)	1:1 $PhAsI_2$:25% eth.EA	5	2	-1.90 ± 0.12
$PhAsI_2 \cdot$py(s)	25% eth.EA	5	3	-102.56 ± 1.64
γ-pico(l)	1:1 $PhAsI_2$:25% eth.EA	5	2	-1.76 ± 0.09
$PhAsI_2 \cdot \gamma$-pico(s)	25% eth.EA	5	3	-56.89 ± 0.30

[a] eth., ethanolic; EA, ethanolamine.

Calorimetric measurements

The standard enthalpies of dissolution of the phenyldihaloarsines, ligands and complexes ($\Delta_i H^{\ominus}$) were obtained as previously reported [9] and are given in Table 6. The uncertainty intervals given in this table are twice the standard deviations of the means of about five replicate measurements on each compound. Combined errors were calculated from the square root of the sum of the squares of the component errors. The standard enthalpies of the acid/base reaction ($\Delta_r H^{\ominus}$) can be determined from the standard enthalpies of dissolution. $\Delta_r H^{\ominus} = \Delta_1 H^{\ominus} + \Delta_2 H^{\ominus} - \Delta_3 H^{\ominus}$ or $\Delta_r H^{\ominus} = \Delta_4 H^{\ominus} + \Delta_5 H^{\ominus} - \Delta_6 H^{\ominus}$.

Using appropriate thermochemical cycles and applying Hess's law, the standard enthalpies of the following reactions were obtained:

$$PhAsX_2 \cdot L(s) = PhAsX_2(g) + L(g) \qquad (\Delta_D H^{\ominus})$$

$$PhAsX_2 \cdot L(s) = PhAsX_2(g) + L(g) \qquad (-\Delta_M H^{\ominus})$$

$$PhAsX_2 \cdot L(g) = PhAsX_2(g) + L(g) \qquad (-\Delta_r H^{\ominus}(g))$$

The $\Delta_r H^{\ominus}(g)$ values can be used to calculate the standard enthalpy of the arsenic–nitrogen bond ($\bar{D}$(As–N)) being equal to $-\Delta_r H^{\ominus}(g)/n$. Table 7 lists the values for all these parameters. For the determination of

TABLE 7

Summary of the thermochemical results (kJ mol^{-1})

Compound	$\Delta_r H^{\ominus}$	$\Delta_f H^{\ominus}$	$\Delta_{s,l}^{g} H^{\ominus}$	$\Delta_M H^{\ominus}$	$\Delta_D H^{\ominus}$	$\Delta_r H^{\ominus}(g)$	$\bar{D}$(As–N)
$AsCl_3$(l)		−305.0 [a]	43.5 [a]				
$AsBr_3$(s)		−197.5 [a]	67.5 [a]				
AsI_3(s)		−58.2 [a]	95.0 [a]				
Ph_3As(s)		408.4 ± 10.5 [b]	98.3 [b]				
$PhAsCl_2$(g)		−36.3 [c]	59.9 [d]				
$PhAsBr_2$(g)		49.5 [c]	77.7 [c]				
$PhAsI_2$(g)		160.6 [c]	96.1 [c]				
py(l)		101.2 ± 0.7 [e]	40.2 ± 0.0 [e]				
γ-pico(l)		58.5 ± 1.1 [e]	45.3 ± 0.4 [e]				
β-pico(l)		61.9 ± 0.5 [e]	44.4 ± 0.0 [e]				
$PhAsCl_2$·py(s)	−52.89 ± 2.05	−47.9		−153.0	93.1 ± 2.05	−112.8	112.8
$PhAsCl_2$·γ-pico(s)	−84.58 ± 2.20	−122.3		−189.8	129.9 ± 2.24	−144.5	144.5
$PhAsBr_2$·py(s)	−106.85 ± 0.97	−33.9		−224.8	147.1 ± 1.0	−184.6	184.6
$PhAsBr_2$·γ-pico(s)	−117.14 ± 0.83	−86.8		−240.1	162.4 ± 0.9	−194.8	194.8
$PhAsBr_2$·β-pico(s)	−107.57 ± 2.13	−73.9		−229.7	152.0 ± 2.1	−185.3	185.3
$PhAsI_2$·py(s)	−75.45 ± 1.82	90.2		−211.8	155.7 ± 1.8	−171.6	171.6
$PhAsI_2$·γ-pico(s)	−120.98 ± 0.83	2.0		−262.4	166.3 ± 0.9	−217.1	217.1

[a] Ref. 14.

[b] Ref. 15.

[c] Ref. 15, see text.

[d] Ref. 16.

[e] Ref. 17.

$\Delta_r H^{\ominus}$(g), it was necessary to assume that the molar standard enthalpy of sublimation of each complex ($\Delta_s^g H^{\ominus}$) is equal to the enthalpy of vaporization of one mole of ligand [9]. The melting points and TG studies showed that the complexes decompose on heating, are unstable in the liquid phase, and are problably also unstable in the gas phase. The hypothesis that the $\Delta_s^g H^{\ominus}$ values of the complexes are equal to the $\Delta_l^g H^{\ominus}$ values of the ligands is the most consistent [9].

To determine the standard enthalpy of formation of the complexes, it was necessary to estimate the standard enthalpies of formation in the gaseous phase of the arsines and the standard enthalpies of vaporization of phenyldibromearsine and phenyldiiodoarsine. These values are not cited in the literature. They were calculated using a group contribution method from the enthalpies of formation of AsX_3 and Ph_3As, and from the enthalpies of sublimation of Ph_3As and AsX_3 [14,15]. The value calculated by this method for the enthalpy of vaporization of $PhAsCl_2$ agrees with the experimental value found in the literature [16].

From the $\Delta_r H^{\ominus}$ values for a series of complexes with the same stoichiometry and the same ligand, the acidity order $PhAsI_2 > PhAsBr_2 > PhAsCl_2$ can be obtained. This order is contrary to the order observed in the trihalide complexes of the same ligands [1]. When the arsine is fixed and the ligands changed for complexes with the same stoichiometry, the basicity order γ-pico > β-pico > py is obtained, which is the same order as found for the trihalide complexes [1]. Based on the $\bar{D}$(As–N) values of the complexes, the same sequences for basicity and acidity are obtained.

The data for $\Delta_r H^{\ominus}$ values and other parameters indicate that the energy of the As–N bond increases in the sequence py < β-pico < γ-pico, as expected [1]. Replacing a halogen with a phenyl group in arsenic trihalides leads to an inversion of the acidity order of the resulting arsines if the thermochemical parameters of the complexes with the same stoichiometry and the same ligands are compared. The mean standard enthalpies of arsenic–nitrogen coordinate bonds for $PhAsCl_2$ complexes are weaker than those for $AsCl_3$ complexes. However they are stronger for $PhAsI_2$ complexes than for AsI_3 complexes. The mean energies of As–N coordinate bonds in phenyldihaloarsine complexes range from 113 to 217 kJ mol^{-1}.

ACKNOWLEDGEMENTS

The author thanks CNPq for financial support and Fundação Banco do Brasil for financial support of part of this work.

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